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Introducing Chemical Transport Selectivity into Gold Nanotubule Membranes

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Abstract

We recently described polymeric membranes that contain a collection of monodisperse Au nanotubules with inside diameters of molecular dimensions (<1 nm). We showed that these membranes can be used to cleanly separate small molecules on the basis of molecular size. These membranes can also show charge-based transport selectivity which can be reversible switched between cation and anion-selective states. In addition to molecular size- and charge-based selectivity, chemical interactions (e.g., hydrogen bonding or hydrophobic interactions) between the membrane material and the molecule to be transport can be used to control transport selectivity. The introduction of such chemically-based transport selectivity into the Au nanotubule membranes is described here. This was accomplished by chemisorbing thiols (R-SH) to the Au tubule surfaces. Membranes derivatized with two different R groups - the hydrophobic $R = -C_{16}H_{33}$ and the more hydrophilic $R = -C_2H_4-OH$ - were prepared. We show here that the rate and selectivity of transport in these membranes is dramatically altered by the chemical identity of the R group.

Membrane-based chemical separations are potentially more economical and less energy intensive than competing separations technologies (1). However, higher transport selectivities will be required if membranes are to make greater inroads into industrial chemical and bioseparations. We recently described polymeric membranes that contain a collection of monodisperse Au nanotubules with inside diameters of molecular dimensions (<1 nm) (2,3). We showed that these membranes can be used to cleanly separate small molecules on the basis of molecular size (2). These membranes can also show charge-based transport selectivity which can be reversible switched between cation and anion-selective states (3).

In addition to molecular size- (2) and charge- (3) based selectivity, chemical interactions (e.g., hydrogen bonding or hydrophobic interactions) between the membrane material and the molecule to be transport can be used to control transport selectivity. For example, the molecular imprinting method has recently been used to prepare membranes that show such *chemically-based* transport selectivity (4,5). The introduction of chemically-based transport selectivity into our Au nanotubule membranes is described, for the first time, here. This was accomplished by chemisorbing thiols (RSH) to the Au tubule surfaces (Eq 1) (6). Membranes derivatized with two different R groups - the hydrophobic R = -$C_{16}H_{33}$ and the more hydrophilic (3) R = -C_2H_4-OH - were prepared. We show here that the rate and selectivity of transport in these membranes is dramatically altered by the chemical identity of the R group.

$$Au| \quad + \quad RSH \text{ -------> } \quad Au|\text{—SR}$$

(1)
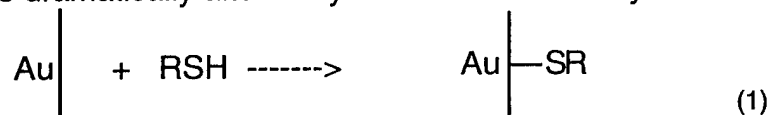
The electroless plating procedure described previously (2,3,7) was used to plate the Au nanotubules into the pores of commercially-available polycarbonate track-etch filters (Osmonics, 6 μm thick, pore diameter = 30 or 50

nm, 6×10^8 pores cm^{-2}). This plating method yields an Au tubule within each pore, and an Au surface layer on each face of the membrane. The plating solution was buffered at pH = 12 and cooled to 5° C. This plating bath yields "bottleneck" tubules (2); i.e. the diameter of the tube that penetrates the Au surface layers is smaller than the diameter that runs through the bulk of the membrane. Bottleneck tubules are preferable from a rate-of-transport (flux) viewpoint, because flux is limited by transport in the constrictions in the thin (~200 nm) Au surface layers rather than down the 6 μm length of the tube (2).

The inside diameter (d) of the nanotubes was varied by varying the plating time, and a gas-flux method was used to obtain approximate d values for each membrane (2,3). Because these tubes are bottleneck in shape, the d-values obtained are a convolution of the diameter of the constriction at the surface, and the larger diameter of the tube that spans the thickness of the membrane (2). In addition, the d values reported here were measured before chemisorption of the thiol (Eq 1), and this will clearly result in further constriction of the pore. Hence, the reported d values are over-estimates; however, highly accurate d values were not required to interpret the data presented here.

After preparation, the Au nanotube membranes were immersed for 12 hours into a 1 mM solution of either mercaptoethanol or hexadecylthiol; the solvent was absolute ethanol. This resulted in chemisorption of the desired thiol to all of the Au surfaces (inside Au nanotubule walls plus Au surface layers). That the thiols did, indeed, chemisorb to the inside tubule walls (and not just to the Au surface layers) was proven by determining the transport properties (*vide infra*) of the as-prepared membrane, removing the surface thiol layers by exposure to an oxygen plasma (8), and redetermining the transport properties. The rate and selectivity of transport was the same before and after removal of the thiol on the surfaces of the membrane. The question of how

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these thiols pack onto the inner walls of these nanoscopic tubules is an interesting, and experimentally challenging, issue.

Transport properties were determined by mounting the membrane between the two halves of a U-tube permeation cell (2,3,9). The feed half-cell contained 5 mL of an aqueous solution of the molecule to be transported (the permeant molecule); the permeate half-cell initially contained 5 mL of pure water. Both half-cells were vigorously stirred to prevent solution concentration polarization. The transport of the permeant molecule from the feed half-cell, through the membrane, and into the permeate half-cell was monitored by periodically assaying (via UV absorbance spectroscopy) the permeate solution. The permeation data obtained were processed as plots of moles of permeant molecule transported (per cm^2 of geometric membrane area) vs. time (Figures 1 and 2); the slope provides the permeant flux.

Au nanotube membranes with the following approximate (*vide supra*) nanotube diameters were prepared: d = 28±1 nm, 7.0±0.1 nm, 1.9±0.1 nm and 1.5±0.2 nm (10). Figure 1 shows permeation data for transport of pyridine through these various membranes. Data for membranes derivatized with both the R = -C_2H_4-OH - (upper solid curve) and the R = -$C_{16}H_{33}$ (lower dashed curve) thiols are shown. The corresponding flux data are shown in Table I. As would be expected (11), the flux of pyridine decreases with decreasing tubule diameter for both the R = -C_2H_4-OH - and R = -$C_{16}H_{33}$ membranes. However, for any nanotube diameter, the pyridine flux in the R = -C_2H_4-OH membrane is greater than in the R = -$C_{16}H_{33}$ membrane. In addition, as the tubule diameter decreases, the difference in flux between the R = -C_2H_4-OH and the R = -$C_{16}H_{33}$ membranes becomes more dramatic (Table I).

This last point can be illustrated by defining a selectivity coefficient, $\alpha_{OH/C16}$, which is the flux of pyridine in the R = -C_2H_4-OH membrane divided

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by the flux of pyridine in the corresponding R = -C$_{16}$H$_{33}$ membrane (12). As shown in Table I, this selectivity coefficient increases with decreasing tubule diameter. The smallest tubule-diameter R = -C$_2$H$_4$-OH-membrane showed a factor of 23 higher selectivity for pyridine transport than the corresponding R = -C$_{16}$H$_{33}$ membrane. Similar large $\alpha_{OH/C16}$ values were obtained for two other relatively hydrophilic organic molecules - benzoic acid ($\alpha_{OH/C16}$ = 28) and phenol ($\alpha_{OH/C16}$ = 15).

Results of analogous permeation studies for the hydrophobic toluene molecule are shown in Figure 2. Now the opposite selectivity pattern is observed; i.e., toluene is preferentially transported in the R = -C$_{16}$H$_{33}$ membranes. This can be illustrated by defining the alternative selectivity coefficient $\alpha_{C16/OH}$, which is the flux of toluene in the R = -C$_{16}$H$_{33}$ membrane divided by the flux of toluene in the corresponding R = -C$_2$H$_4$-OH membrane (Table I) (12). As was the case for $\alpha_{OH/C16}$, the $\alpha_{C16/OH}$ values increase with decreasing tubule diameter. In addition to toluene, $\alpha_{C16/OH}$ values were determined for p-xylene and naphthalene in the d = 1.9 nm membranes. These molecules increase in hydrophobicity in the order toluene < p-xylene << naphthalene, and the $\alpha_{C16/OH}$ values obtained were - toluene 2.8, p-xylene 6.2, and naphthalene 16.

We suggest the following interpretation for these various data: Note first that of all the flux values reported in Table I, the toluene fluxes in the R = -C$_{16}$H$_{33}$ membranes are, in general, the highest. This may, at first glance, seem surprising because the long C$_{16}$ thiol might be expected to hinder diffusion in these membranes (13). However, flux is proportional to both the diffusion coefficient and *the partition coefficient* for the permeant molecule in the membrane (14). The comparison of $\alpha_{C16/OH}$ values for toluene, p-xylene, and naphthalene clearly shows that the hydrophobic effect causes preferential

partitioning of hydrophobic molecules into these hydrophobic membranes. Hence, we suggest that flux for hydrophobic molecules in the $R = -C_{16}H_{33}$ membranes is driven by favorable partitioning of such molecules from water (the feed solution) into the membrane.

This hypothesis is supported by the fact that the expected (11) decrease in flux with tubule diameter is not, in general, observed for toluene in the $R = -C_{16}H_{33}$ membranes (Table I). This clearly indicates that something besides diffusivity is strongly influencing the flux. This hypothesis also is supported by the fact that the next largest group of flux values in Table I is for toluene in the $R = -C_2H_4-OH$ membranes. Water can still lower its free energy by partitioning the hydrophobic toluene molecule into these membranes, but much of the advantage is lost due to the lower hydrophobicity of the $R = -C_2H_4-OH$ group relative to $R = -C_{16}H_{33}$. Because of this diminution in the hydrophobic push, toluene fluxes are lower in the $R = -C_2H_4-OH$ membranes than in the $R = -C_{16}H_{33}$ membranes (Table I).

The next highest set of fluxes is for pyridine in the $R = -C_2H_4-OH$ membranes (Table I). Clearly, the hydrophobic push for this molecule is greatly diminished relative to toluene, and this accounts for the lower pyridine (vs. toluene) fluxes in the $R = -C_2H_4-OH$ membranes. Finally, the lowest fluxes are for pyridine in the $R = -C_{16}H_{33}$ membranes. Now the relatively hydrophilic pyridine molecule pays an enthalpic penalty (loss of hydration) upon entering these hydrophobic membranes. We suggest that this results in a low partition coefficient and correspondingly low fluxes.

The data presented here show that thiol chemisorption dramatically alters the transport properties of the Au nanotubule membranes. We have interpreted these data in terms of the effect of the thiol on partitioning of the permeant molecule into the membrane. Finally, the ratio of the fluxes for

toluene vs. pyridine transport in the d=1.5 nm R = -C$_{16}$H$_{33}$ membrane is greater than 400 (Table I). This suggests that this membrane should be very good at separating mixtures containing hydrophobic and hydrophilic molecules, with the hydrophobic molecules being transported to the permeate and the hydrophilic molecules being retained in the feed. We are currently exploring this possibility.

References and Notes

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6. The structure on the left of Eq 1 represents an Au surface. See, e.g., Porter, M.D.; Bright, T.B.; Allara, D.L.; Chidsey, C.E.D. *J. Am. Chem. Soc.* 1987, *109*, 3559-3568.

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10. Standard deviations reflect ≥3 gas-flux measurements for each membrane.

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12. Selectivity coefficients are typically defined as the ratio of fluxes for two different molecules in the same membrane. Here we define the selectivity coefficient as the ratio of fluxes of the same molecule in two different membranes.

13. The mechanism of diffusion of these permeant molecules in these membranes is an issue that must be explored in detail. We have shown (3) that the R = $-C_2H_4-OH$-derivatized nanotubes flood when immersed in water. In contrast, permeation experiments with inorganic salts suggest that the R = $-C_{16}H_{33}$ nanotubes do not flood with water.

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Table I. Pyridine and toluene flux and selectivity data.

Permeant Molecule	Nanotube Diameter (nm)	Flux in the $R = -C_2H_4-OH$ Membranes (mole cm^{-2} hr^{-1})	Flux in the $R = -C_{16}H_{33}$ Membranes (mole cm^{-2} hr^{-1})	$\alpha OH/C16$	$\alpha C16/OH$
Pyridine	28	3.7×10^{-3}	2.6×10^{-3}	1.4	-
Pyridine	7	9.7×10^{-4}	3.5×10^{-4}	2.8	-
Pyridine	1.9	2.5×10^{-4}	2.2×10^{-5}	11	-
Pyridine	1.5	1.2×10^{-4}	5.2×10^{-6}	23	-
Toluene	28	2.4×10^{-3}	2.9×10^{-3}	-	1.2
Toluene	7	2.7×10^{-3}	5.5×10^{-3}	-	2.0
Toluene	1.9	1.3×10^{-3}	3.6×10^{-3}	-	2.8
Toluene	1.5	4.2×10^{-4}	2.1×10^{-3}	-	5.0

Figure Captions

Figure 1. Pyridine permeation data for membranes containing Au nanotubes with approximate inside diameters of (A) 28±1 nm, (B) 7.0±0.1 nm, (C) 1.9±0.1 nm, and (D) 1.5±0.2 nm. In each case, the upper solid line is for the R = -C_2H_4-OH membrane and the lower dashed line is for the R = -$C_{16}H_{33}$ membrane.

Figure 2. Toluene permeation data. Membranes as per Figure 1. In each case, the upper dashed line is for the R = -$C_{16}H_{33}$ membrane and the lower solid line is for the R = -C_2H_4-OH membrane.
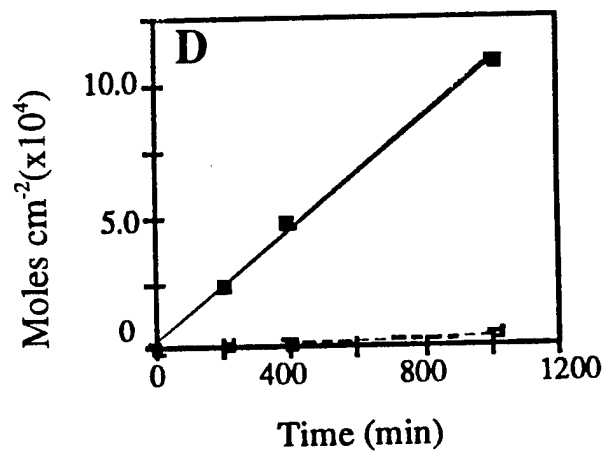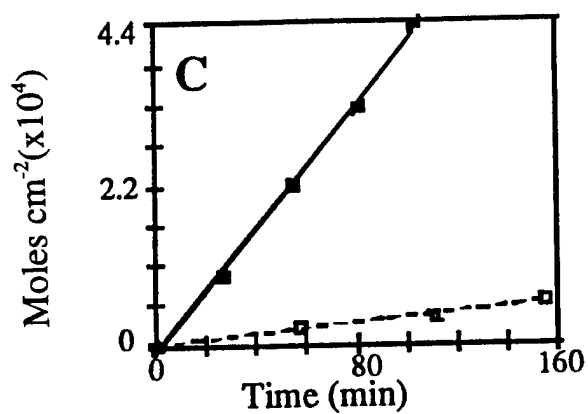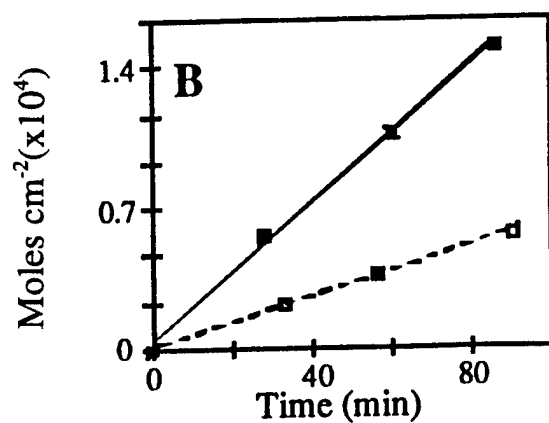
A — Moles cm⁻²(×10³) vs Time (min)
B — Moles cm⁻²(×10⁴) vs Time (min)
C — Moles cm⁻²(×10⁴) vs Time (min)
D — Moles cm⁻²(×10⁴) vs Time (min)

Fig 1

Fig 2